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Computed Barrier Heights for



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Abstract. The barrier heights (including zero-point effects) for $\text{H} + \text{CH}_2\text{O} \rightarrow \text{CH}_3\text{O}$ and $\text{CH}_3\text{O} \rightarrow \text{CH}_2\text{OH}$ have been computed using complete active space self consistent field (CASSCF)/ gradient calculations to define the stationary point geometries and harmonic frequencies and internally contracted configuration-interaction (CCI) to refine the energetics. The computed barrier heights are 5.6 kcal/mol and 30.1 kcal/mol, respectively. The former barrier height compares favorably to an experimental activation energy of 5.2 kcal/mol.

The CH_3O radical is important in combustion and atmospheric chemistry [1]. In addition, recent experiments have studied individual rovibrational states of CH_3O above the $\text{H}-\text{CH}_2\text{O}$ dissociation threshold by stimulated emission pumping [3]. The interpretation of these experiments depends critically on the barriers to decomposition of CH_3O to $\text{H} + \text{CH}_2\text{O}$ and rearrangement to CH_2OH . Previous studies of these barrier heights include the work of Saebø, Radom, and Schaefer [2], who used Møller-Plesset perturbation theory through third order with small basis sets up through 6-31G**. More recently, Page, Lin, He, and Choudhury [4] reported somewhat more accurate calculations using multireference configuration-interaction (MRCI) with polarized triple zeta basis sets. In the present paper more accurate calculations are reported which make use of larger basis sets and extensive CI.

Two different basis sets were used in this work. For the complete active space self consistent field (CASSCF) gradient calculations the polarized double zeta set of Dunning and Hay [5] was used. The basis set for C and O is a (9s5p)/[3s2p] basis augmented by a single set of 3d functions with exponents of 0.75 and 0.85 for C and O, respectively. The H basis is (4s)/[2s] augmented with a single set of 2p functions with exponent 1.00. The basis set used in the CI calculations is the Dunning correlation consistent triple zeta double polarization basis set [6]. This basis is [4s3p2d1f] for C and O and [3s2p1d] for H and is described in detail in Ref. 6.

The calculations were carried out in C_s symmetry for a wavefunction of $^2A'$ symmetry. From the Hessian matrix in the diagonal representation, the stationary points obtained in C_s symmetry are the minimum for $\text{CH}_2\text{O} + \text{H}$, the saddle point for $\text{CH}_2\text{O} + \text{H} \rightarrow \text{CH}_3\text{O}$, the CH_3O minimum, and the saddle point for $\text{CH}_3\text{O} \rightarrow \text{CH}_2\text{OH}$. For CH_3O the $^2A'$ state corresponds to one component of the 2E state in C_{3v} symmetry. According to the calculations of Saebø et al. [2], the Jahn-Teller stabilization energy in this system is 0.56 kcal/mol and the Jahn-Teller splitting is 0.12 kcal/mol, with the $^2A'$ component lower. CH_2OH is found to have no symmetry and the use of a mirror plane of symmetry would not be appropriate. However, the separation between CH_3O and CH_2OH has been accurately computed by Bauschlicher, Langhoff, and Walch [7] and further calculations for CH_2OH were not carried out here.

The CASSCF calculations consisted of five electrons and five orbitals. The active electrons for CH_3O included the CO bond pair, one CH bond pair (the CH bond in the molecular plane), and the a' O 2p like orbital. These orbitals correspond to the CO σ and π bonds plus a H 1s orbital for $\text{CH}_2\text{O} + \text{H}$. The remaining electrons, which are inactive, include the other two CH bond pairs, the a'' O 2p like orbital and the O 1s, O 2s, and C 1s like orbitals. In generating the set of reference configurations for the subsequent internally contracted CI (CCI) calculations, no more than two electrons were permitted in the weakly occupied CASSCF orbitals. All but the O 1s and C 1s electrons were correlated in the CCI calculation. A multi-reference analog of Davidson's correction [8] was added to the CCI energies.

The CASSCF/gradient calculations used the SIRIUS/ABACUS system of programs [9], while the CCI calculations were carried out with MOLPRO [10,11]. The calculations were carried out on the NASA Ames Cray Y-MP.

Table I gives the harmonic vibrational frequencies, rotational constants, and geometric parameters for the stationary points considered in this work. Here H_a is the H of the spectator CH bonds, while H_b is the hydrogen which transfers during the reaction. The geometries and frequencies in Table I are quite similar to those obtained by Page et al. [4]. This is expected since a CASSCF wavefunction was used in Ref. 4. However, in Ref. 4 the CO σ bond was not correlated. For CH_3O this has the expected effect that the CO bond is elongated by $\approx 0.03 \text{ \AA}$ compared to the calculations in Ref. 4. At the H- CH_2O saddle point the CO bond is elongated by $\approx 0.02 \text{ \AA}$ and the C- H_b bond is shorter by $\approx 0.05 \text{ \AA}$ as compared to Ref 4. There are larger differences between this work and the results of Saebø et al. Here the geometry for CH_3O is similar except for the expected elongation of the C- H_b and CO bonds. However, there are significant differences in the geometry of the H- CH_2O saddle point. In particular, the C- H_b bond length is shorter by $\approx 0.18 \text{ \AA}$. This result is consistent with the expectation that saddle point geometries will be more sensitive to electron correlation effects than will stationary points.

Table II gives the computed energies and zero-point corrections. The energies are from the CCI calculations, while the zero-point corrections are derived from the CASSCF harmonic frequencies. From Table II it is seen that the relative energies are only very slightly changed ($\approx 0.1 \text{ kcal/mol}$) in going from the [4s3p2d1f/3s2p1d]

basis set to the [5s4p3d2f/4s3p2d] basis set. Table III compares the computed barrier heights obtained in the present calculations to those obtained by Saebø et al. [2] and by Page et al. [4]. Here it is seen that the barriers obtained by Saebø et al. are too large by ≈ 6 kcal/mol., while the barrier for $\text{H} + \text{CH}_2\text{O} \rightarrow \text{CH}_3\text{O}$ obtained by Page et al. is 2.3 kcal/mol larger than in the present calculations. Our computed barrier height is 5.6 kcal/mol for $\text{H} + \text{CH}_2\text{O} \rightarrow \text{CH}_3\text{O}$ and 5.2 kcal/mol for $\text{D} + \text{CH}_2\text{O} \rightarrow \text{CDH}_2\text{O}$. This result is in good agreement with experimental estimated activation energies of 5.2 kcal/mol for $\text{H} + \text{CH}_2\text{O}$ and 3.9 kcal/mol for $\text{D} + \text{H}_2\text{CO}$ [12].

It is concluded that the present calculations give energetics for the CH_3O system which are of chemical accuracy (in this case the estimated error bars are ± 1 kcal/mol). This is in contrast to results obtained by Saebø et al. using Møller-Plesset perturbation theory, where the errors in the computed barrier heights are ≈ 6 kcal/mol.

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Table I. Computed stationary point harmonic frequencies (cm^{-1}), rotational constants (cm^{-1}), bond lengths (\AA), and bond angles (degrees).

	CH_3O	$\text{CH}_3\text{O} \rightarrow \text{CH}_2\text{OH}$	$\text{H-CH}_2\text{O}$	$\text{H} + \text{CH}_2\text{O}$
ω_1	3216	3261	3190	3174
ω_2	2921	2378	1657	1766
ω_3	1608	1556	1471	1589
ω_4	1471	1101	1220	1213
ω_5	1103	1037	605	
ω_6	997	2254 <i>i</i>	1435 <i>i</i>	
ω_7	3284	3391	3297	3272
ω_8	1491	1159	1281	1304
ω_9	1050	1015	770	
A	5.180	5.718	3.927	9.548
B	0.885	0.929	1.007	1.263
C	0.884	0.900	0.962	1.115
r_{C-H_a}	1.092	1.086	1.094	1.097
r_{C-H_b}	1.122	1.275	1.668	
r_{C-O}	1.412	1.418	1.259	1.226
r_{O-H_b}		1.237	2.292	
$\angle \text{H}_a\text{CH}_a$	111.5	119.1	117.1	117.2
$\angle \text{H}_a\text{CH}_b$	108.2	117.1	91.2	
$\angle \text{H}_a\text{CO}$	111.7	116.5	120.3	121.4
$\angle \text{H}_b\text{CO}$	105.3	54.4	102.2	

Table II. Computed energies and zero-point corrections.

	zero-point energy ^a	[4s3p2d1f/3s2p1d] basis Energy ^b	ΔE^c	[5s4p3d2f/4s3p2d] basis Energy ^b	ΔE^c
CH ₃ O	0.03905	-114.84037(-.86976)	0.0	-114.86388(-.89511)	0.0
CH ₃ O \rightarrow CH ₂ OH	0.03394	-114.78503(-.81666)	30.1	-114.80875(-.84226)	30.0
H-CH ₂ O	0.03074	-114.79504(-.82416)	23.4	-114.81873(-.84963)	23.3
H + CH ₂ O	0.02806	-114.80390(-.83039)	17.8		

^a energy in E_H.

^b energy in E_H. The first energy is for CCI, while the energy given in parenthesis is for CCI + Q and is relative to -114. E_H.

^c relative energy in kcal/mol. The energies are from CCI + Q (i.e. including a multi-reference Davidson's correction) and include zero-point energy.

Table III. Comparison of computed barrier heights (kcal/mol).

	Saebø et al. ^a	Page et al. ^b	PW ^c	Exp.
$\text{H} + \text{CH}_2\text{O} \rightarrow \text{CH}_3\text{O}$	12.5	8.0	5.6	5.2 ^d , 6.2 ^e
$\text{D} + \text{CH}_2\text{O} \rightarrow \text{CDH}_2\text{O}$			5.2	3.9 ^d , 4.8 ^e
$\text{CH}_3\text{O} \rightarrow \text{CH}_2\text{OH}$	36.0		30.1	

^a Reference 2.

^b Reference 4.

^c Present work.

^d Estimated activation energy from a room temperature rate constant for $\text{D} + \text{H}_2\text{CO}$, an assumed preexponential factor of $2 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$, and a zero-point energy difference between $\text{D} + \text{H}_2\text{CO}$ and $\text{H} + \text{H}_2\text{CO}$ of $\approx 1.3 \text{ kcal/mol}$. Ref. 12.

^e Estimated threshold energy from an RRKM analysis. Ref. 12.